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Recovery of Vanadium, Uranium, and Phosphate From Idaho Phosphorite Ores

By J. C. Judd, R. G. Sandberg, and J. L. Huiatt

UNITED STATES DEPARTMENT OF THE INTERIOR

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	mV	millivolt
ft	foot	pct	percent
g	gram	ppm	part per million
g/L	gram per liter	psi	pound per square inch
h	hour	rpm	revolution per minute
L	liter	st	short ton
lb/st	pound per short ton	st/yr	short ton per year
min	minute	vol pct	volume percent
M	molar	wt pct	weight percent
mL	milliliter		

RECOVERY OF VANADIUM, URANIUM, AND PHOSPHATE FROM IDAHO PHOSPHORITE ORES

By J. C. Judd,[1] R. G. Sandberg,[2] and J. L. Huiatt[3]

ABSTRACT

The Bureau of Mines investigated the recovery of vanadium, uranium, and phosphorus from low-grade phosphorite ores and concentrate by leaching with H_2SO_4. Samples containing 0.12 to 0.23 pct V_2O_5, 0.009 to 0.012 pct U_3O_8, and 18 to 30 pct P_2O_5 were treated by batch-agitation leaching, roasting followed by acid leaching, salt-roasting followed by acid leaching, and leaching under pressure.

Maximum recoveries using leaching alone ranged from 78 to 98 pct of the V_2O_5 and 74 to 88 pct of the U_3O_8. Leaching under pressure resulted in extractions of 88 to 95 pct of the V_2O_5 and 84 to 89 pct of the U_3O_8. Leaching following roasting--with or without NaCl--produced extractions of 97 to 99 pct of the V_2O_5 and 86 to 91 pct of the U_3O_8. Depending on the technique(s) employed, phosphate extractions ranged from 89 to 99 pct.

Solvent extraction laboratory tests were conducted to selectively recover vanadium and uranium values from acid leach solutions. An average of 95 pct of the U_3O_8 was recovered using di(2-ethylhexyl)phosphoric acid, plus trioctylphosphinic oxide. Essentially all of the V_2O_5 was recovered with octylphenyl acid phosphate plus isodecanol. The phosphate remained in the raffinate.

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INTRODUCTION

Vanadium is classified as a strategic and critical material because of its significant import dependence and essential use in equipment for defense, energy, and transportation (1).[4] It is principally consumed by the iron and steel industry as ferrovanadium or related vanadium-carbon ferroalloys. Vanadium significantly increases strength and improves toughness and ductility of carbon steels, which are used for constructing high-rise buildings, bridges, and pipelines. Other important applications for vanadium are as additives to titanium-based alloys, which are consumed in jet engines and other aircraft parts, and as catalysts, which are used in the manufacturing of sulfuric acid and other chemicals.

Vanadium is widely distributed throughout the earth but in rather low concentration. In the United States, particularly in the West, vanadium is found in uranium-bearing minerals and in certain phosphatic shales and phosphate rocks. One of these phosphatic deposits, located in Idaho, represents a large domestic vanadium reserve. The phosphorite beds, generally 3 to 20 ft thick, average 20 to 32 pct P_2O_5 and 0.14 pct V_2O_5. At least 125,000 short tons (st) of coproduct vanadium is contained in these deposits. An additional 1.6 million st of coproduct vanadium occurs in marginal reserves of phosphatic shale and low-grade phosphorite dispersed in the northern Rocky Mountains (1).

The western phosphate industry processes 2.6 million st/yr ore (2). Following beneficiation, the plus 325-mesh concentrate (30 to 32 pct P_2O_5) is leached with H_2SO_4, and the minus 325-mesh material is rejected to the tailings. A significant amount of vanadium and uranium is lost with the rejected tailings. Phosphoric acid (H_3PO_4) is produced from concentrates by either the dihydrate process (at temperatures of <80° C) or the hemihydrate process (at >80° C). The P_2O_5 content of the acid is 28 to 30 pct with the dihydrate process and 45 to 54 pct with the hemihydrate process. If necessary, evaporation is used to increase the P_2O_5 content to 50 to 54 pct, regardless of which process is used (3-4). The chemical equation for the dihydrate (A) and hemihydrate (B) reactions are given below (4-6):

$$3Ca_3(PO_4)2\cdot CaF_2 + 10H_2SO_4 + 20H_2O \rightleftharpoons 6H_3PO_4 + 2HF + 10(CaSO_4\cdot 2H_2O) \quad (A)$$

$$3Ca_3(PO_4)2\cdot CaF_2 + 10H_2SO_4 + 5H_2O \rightleftharpoons 6H_3PO_4 + 2HF + 10(CaSO_4\cdot 1/2H_2O) \quad (B)$$

The approximate amount of H_2SO_4 used for maximum conversion to H_3PO_4 is the stoichiometric amount required to convert the CaO content of the concentrate to $CaSO_4$, plus an additional 2 to 3 pct. Acid concentration is very critical because, if the free sulfate content is too low, the gypsum ($CaSO_4\cdot 2H_2O$) crystals do not grow properly; this affects the rate of filtration (6). Also, the HPO_4 ions are substituted for SO_4 ions in the $CaSO_4$ lattice; this represents a significant P_2O_5 loss. The extent of substitution decreases with H_2SO_4 excess and increases with increased P_2O_5 concentration. Substitution of P_2O_5 in gypsum is also related to solids content in suspension. If the H_2SO_4 concentration is too high, an insoluble $CaSO_4$ layer forms around the particles to be digested (6).

Acid processes for recovery of uranium and vanadium from the usual western resources are similar to those processes used in the production of H_3PO_4, except the feed generally has not been beneficiated prior to U_3O_8 and V_2O_5 recovery. One benefit of processing unbeneficiated phosphorite ore is the elimination of one solid waste stream and the significant problems in its handling (7-8). A second benefit is higher recoveries, as value losses during beneficiation are generally significant. A third benefit is conservation of the resource, as more

[4]Underlined numbers in parentheses refer to items in the list of references at the end of this report.

phosphate should be available per short ton of phosphorite ore mined. Therefore, processing of phosphorite to recover vanadium and uranium requires that phosphorus also be recovered, in order to offset the costs of additional H_2SO_4 consumption.

Because of the strategic importance of vanadium the Bureau of Mines conducted an investigation to recover vanadium, uranium, and phosphorus from unbeneficiated Conda and Fort Hall (Gay Mine) ores, a Conda high-magnesium material, and a Conda concentrate (Simplot Mill). Extraction techniques investigaced were batch-agitation leaching alone; roasting or salt-roasting followed by leaching; and leaching under pressure. Tests were performed to determine acid addition, temperature, solids content, and time requirements for optimum extractions. Complementary solvent extraction tests were conducted to selectively extract the vanadium and uranium from the leach solutions. Solvent extraction was selected because it has been used successfully in the past to recover uranium (4) and vanadium (9) with trioctylphosphinic oxide (TOPO) and to recover both vanadium and uranium (10) with trialkylphosphine oxide plus an alkyl-substituted diaryl phosphoric acid.

SAMPLE DESCRIPTION AND PROCEDURES

SAMPLE DESCRIPTION

The four samples used in this study were designated as Conda, Conda (high-Mg), and Fort Hall ores, and Conda concentrate. Conda and Fort Hall ore samples were from ore deposits that are presently being processed to produce phosphate fertilizer. The Conda concentrate, as received, was a deslimed, calcined product. Ninety-seven percent of this material was minus 35 mesh. The Conda (high-Mg) ore sample represents material that is presently being rejected because its high magnesium content causes processing problems. Chemical and inductively coupled plasma (ICP) analyses of the four samples are listed in tables 1 and 2, respectively.

Microscopic and X-ray diffraction examination identified the samples as calcium phosphate shale or phosphorite. X-ray diffraction also revealed that (1) Conda and Fort Hall samples contained illite clay, quartz, clinozoisite-epidote (a mineral with composition intermediate to these two minerals), limonite, calcite, plagioclase, pyrite, and apatite, and (2) the Conda (high-Mg) sample contained dolomite, apatite, quartz, calcite, and plagioclase. Neither fluorescence nor a Geiger counter could detect any uranium in the four samples, nor could specific vanadium or uranium minerals be identified.

Ore samples were prepared for leaching by pulverizing to minus 35 mesh and

TABLE 1. - Chemical analyses of phosphorite samples, percent

Material	Phosphorite samples			
	Conda	Fort Hall	Conda (high-Mg)	Conda concentrate
V_2O_5	0.164	0.227	0.105	0.12
U_3O_8	.009	.010	.007	.012
P_2O_5	24.9	24.7	18.8	30
Fe_2O_3	1.28	1.24	1.27	.66
MgO	2.51	1.08	5.58	.61
CaO	35.8	35.4	33.6	44.7
SiO_2	17.4	19.8	14.7	12.2
Organic carbon	2.2	3.4	.7	.05

TABLE 2. - Analyses of ore and concentrate samples by inductively coupled plasma (ICP) spectrometry, percent

Element	Conda	Fort Hall	Conda (high-Mg)	Conda concentrate
Al	1.7	1.3	0.93	0.39
Ba	.01	.014	.01	.007
Cd	.01	.014	<.01	.002
Co	.001	.002	<.001	.003
Cr	.08	.09	.06	.033
Cu	.008	.009	.007	.009
Mn	.009	.01	.01	.01
Mo	.008	.013	<.01	.006
Ni	.025	.018	.01	.012
Pb	.001	.005	<.01	.001
Th	.03	.03	<.05	.06
Ti	.11	.11	.054	.169
Zn	.15	.19	.10	.066

TABLE 3. - Wet-screen analyses of Conda ore

Mesh size	Wt pct	Analysis, pct			Distribution, pct		
		V_2O_5	U_3O_8	P_2O_5	V_2O_5	U_3O_8	P_2O_5
Minus 35 plus 48	7.9	0.093	0.011	32.5	4.9	9.5	10.8
Minus 48 plus 65	10.8	.095	.011	29.4	6.9	13	13.5
Minus 65 plus 100	12.1	.090	.012	32	7.4	15.4	16.4
Minus 100 plus 150	7.7	.080	.012	32	4.2	9.5	10.4
Minus 150 plus 200	7.7	.075	.013	31.6	3.9	10.3	10.2
Minus 200	53.8	.20	.007	17	72.7	42.3	38.7
Calculated head	100	.148	.0094	23.7	100	100	100
Assay head	NAp	.164	.0091	24.9	NAp	NAp	NAp

NAp Not applicable.

splitting into 100-g samples. Concentrate samples were screened through minus 35 mesh; the oversize was pulverized to minus 35 mesh. The screen fractions were recombined and split into 100-g samples.

A wet-screen analysis was performed to determine the distribution of vanadium, uranium, and phosphate in the screen fractions from each of the samples. Results of the wet-screen analysis are listed in tables 3-6. The results show 59 to 73 pct of the V_2O_5, 27 to 42 pct of the U_3O_8, and 20 to 39 pct of the P_2O_5 in the ores were distributed to the fines (minus 200-mesh fraction). The Conda concentrate was not considered, as it had already been beneficiated and calcined. The analyses indicate that significant amounts of vanadium, uranium, and phosphate could be lost if the fines are removed during beneficiation.

The Conda concentrate contains less vanadium but more phosphate than the Conda and Fort Hall ore samples. Vanadium and phosphate content are lowest in the Conda (high-Mg) ore. The magnesium content of the Conda (high-Mg) ore is twice the amount in the Conda ore, and five times the amount in the Fort Hall ore.

EXPERIMENTAL PROCEDURES

Leaching procedures used in this study were as follows: batch-agitation leaching; roasting, with and without salt addition, followed by leaching; and leaching under pressure. The lixiviant in all

TABLE 4. - Wet-screen analyses of Fort Hall ore

Mesh size	Wt pct	Analysis, pct			Distribution, pct		
		V_2O_5	U_3O_8	P_2O_5	V_2O_5	U_3O_8	P_2O_5
Minus 35 plus 48.....	13.6	0.17	0.012	28.3	10.1	15.8	16.5
Minus 48 plus 65.....	15.5	.16	.011	29.2	10.8	16.5	19.4
Minus 65 plus 100....	16.5	.14	.011	30.5	10.1	18.9	21.4
Minus 100 plus 150...	9.1	.13	.012	31.8	5.2	10.9	12.4
Minus 150 plus 200...	8	.14	.012	29.7	4.9	10	10.2
Minus 200.....	37.3	.36	.007	12.6	58.9	27.9	20.1
Calculated head.....	100	.228	.0099	23.4	100	100	100
Assay head.....	NAp	.227	.010	24.7	NAp	NAp	NAp

NAp Not applicable.

TABLE 5. - Wet-screen analyses of Conda (high-Mg) material

Mesh size	Wt pct	Analysis, pct			Distribution, pct		
		V_2O_5	U_3O_8	P_2O_5	V_2O_5	U_3O_8	P_2O_5
Minus 35 plus 48.....	17.2	0.07	0.008	22.4	11.7	18.7	20.8
Minus 48 plus 65.....	15.4	.07	.009	23	11.1	21	19.1
Minus 65 plus 100....	12.6	.07	.010	22.3	9.3	17.6	15.1
Minus 100 plus 150...	6.4	.06	.008	23.4	4.2	7.9	8.1
Minus 150 plus 200...	7.1	.06	.007	23.7	4	7.4	9
Minus 200.....	41.3	.14	.005	12.5	59.7	27.4	27.9
Calculated head.....	100	.097	.007	18.5	100	100	100
Assay head.....	NAp	.105	.007	18.8	NAp	NAp	NAp

NAp Not applicable.

TABLE 6. - Wet-screen analyses of Conda concentrate

Mesh size	Wt pct	Analysis, pct			Distribution, pct		
		V_2O_5	U_3O_8	P_2O_5	V_2O_5	U_3O_8	P_2O_5
Minus 35 plus 48.....	4	0.07	0.012	32.3	2.6	4.0	4.1
Minus 48 plus 65.....	6.1	.08	.012	35	4.5	6	6.6
Minus 65 plus 100....	10.4	.08	.012	35.5	8.1	10.6	11.5
Minus 100 plus 150...	9.7	.08	.013	34.1	7.7	10.2	10.4
Minus 150 plus 200...	15.6	.09	.013	34	12.7	16.2	16.5
Minus 200 plus 325...	17.5	.09	.012	32.6	15.4	17.5	17.8
Minus 325.....	36.7	.14	.012	28.8	49	35.5	33.1
Calculated head.....	100	.11	.012	32	100	100	100
Assay head.....	NAp	.12	.012	30	NAp	NAp	NAp

NAp Not applicable.

tests was reagent-grade sulfuric acid (H_2SO_4).

Batch-agitated leach tests were performed using 100 g of minus 35-mesh samples. The samples were leached for 3 to 24 h in a 1,000-mL tall beaker equipped with a reflux tube and stopper. Agitation was accomplished using a custom-fabricated impeller rotated at sufficient speed to maintain particle suspension. A hotplate equipped with a temperature probe was used to keep leach temperatures within ±1° C. After leaching, the slurry was filtered through a Buchner funnel and the residue washed three times using about 50 mL of wash solution per wash. The first wash solution was a dilute solution of H_2SO_4 (pH adjusted to 1.5). Deionized water was used for the second and third washes.

Roast-leach tests were performed by preroasting the ore sample, mixed with or without NaCl, in a muffle furnace. The samples were heated at a specific temperature for 4 h, removed from the furnace, cooled to ambient temperature, and leached for 18 h at 75° C using H_2SO_4 solution.

Pressure-leach tests were performed on 50-g charges of minus 35-mesh material using a glass-lined pressure reaction apparatus equipped with stirrer and temperature probe. The reactor was purged for 5 min with oxygen before heating to the operating temperature. At the end of testing, the reactor was quenched in cold water. The slurry was filtered through a Buchner funnel and washed using a procedure similar to that described for the leach-only tests, except 25 mL of wash solution was used per wash.

The pH and emf values were measured on the terminal leach solution (leach filtrate before wash water was added). The emf values were determined with platinum and saturated-calomel electrodes; the highest values indicate the most highly oxidized solution. Leaching efficiency was assessed by determining and comparing V_2O_5, U_3O_8, and P_2O_5 extractions.

LEACH TESTS

BATCH-AGITATION LEACHING

Batch-agitation leach tests were performed using various acid concentrations, solids contents, temperatures, and leaching times. Good agitation with a well-designed impeller was important to obtain reproducible results. Improper mixing during leaching caused temperature gradients, which decreased mass transfer rates between ore particles and leach solutions.

Conda Ore

The best extractions using Conda ore were 97, 87, and 99 pct of the V_2O_5, U_3O_8, and P_2O_5, respectively. These results were achieved by leaching the ore at 40 pct solids for 18 h at 90° C using 2,000 lb/st H_2SO_4 (table 7). Most wet-process phosphoric acid plants operate at a temperature between 75° and 85° C; a range which is most practical for leaching the phosphorite ores (3). Leaching

TABLE 7. - Effect of temperature on acid leaching of Conda and Fort Hall ore samples[1]

H_2SO_4, lb/st	Solids, pct	Temp, °C	Terminal		Extraction, pct		
			pH	emf, mV	V_2O_5	U_3O_8	P_2O_5
CONDA ORE							
1,500.....	40.....	65	1.1	330	84	86	98
		75	1.3	370	86	88	97
		85	1.1	320	90	87	92
		90	1.1	300	92	87	93
	50.....	65	1.2	340	86	88	99
		75	1.1	360	90	87	98
		85	1.2	330	92	87	99
		90	1.3	323	89	87	95
2,000.....	40.....	65	.4	360	85	86	94
		75	.5	345	94	88	98
		85	.4	370	95	87	97
		90	.5	360	97	87	99
FORT HALL ORE							
1,500.....	40.....	65	0.7	320	74	77	92
		75	.9	340	78	74	89
		85	.7	290	84	78	96
		90	.9	350	89	89	98

[1]Conditions: 100 g of minus 35-mesh samples leached for 18 h.

Conda ore at 75° C for 18 h at 40 pct solids using 2,000 lb/st H_2SO_4 extracted 94, 88, and 98 pct of the V_2O_5, U_3O_8, and P_2O_5, respectively (table 8). Increasing the temperature to 85° C had little effect on extraction.

Experiments performed at 75° C and 18-h leaching time (table 8) showed that increasing pulp density from 33-1/3 pct solids to 40 pct solids significantly improved V_2O_5 and P_2O_5 extraction from Conda ore for a given acid concentration, but had little effect on U_3O_8 extraction. Increasing pulp density to 50 pct solids had no significant effect on extraction.

Fort Hall Ore

The best extractions using Fort Hall ore were 89, 89, and 98 pct of the V_2O_5, U_3O_8, and P_2O_5, respectively. These results were achieved by leaching the ore at 40 pct solids for 18 h at 90° C using 1,500 lb/st H_2SO_4 (table 7). Higher temperatures and longer leaching times generally improved extraction from this ore (tables 7 and 9). However, leaching at 85° C lowered V_2O_5, U_3O_8, and P_2O_5 extractions to 84, 78, and 96 pct, respectively, and leaching at 75° C produced still lower results of 78, 74, and 89 pct V_2O_5, U_3O_8, and P_2O_5, respectively. Increasing the acid addition (table 10) from 1,500 to 2,500 lb/st H_2SO_4 (at 75° C) increased phosphate extraction from 89 to 93 pct but in turn reduced U_3O_8 extraction from 74 to 71 pct.

In general, temperature and time had greater effects on extraction than did acid addition. (See tables 7 and 9.) The ore was more difficult to agitate at 2,000 lb/st H_2SO_4 than at either 1,500 or 2,500 lb/st H_2SO_4, which may account for the lower extractions at 2,000 lb/st H_2SO_4 (table 10). The Fort Hall ore could not be agitated at 50 pct solids.

TABLE 8. - Effect of acid concentration and solids content on acid leaching of Conda ore samples[1]

H_2SO_4, lb/st	Terminal		Extraction, pct		
	pH	emf, mV	V_2O_5	U_3O_8	P_2O_5
33-1/3 pct SOLIDS					
1,000....	1.7	350	63	62	71
1,500....	1.4	330	79	85	84
2,000....	.6	350	89	86	92
2,500....	.5	350	81	72	82
3,000....	.2	370	91	86	96
40 pct SOLIDS					
1,000....	1.6	330	65	63	70
1,500....	1.3	370	86	88	97
2,000....	.5	350	94	88	98
2,500....	.2	370	90	75	98
3,000....	.0	380	90	52	90
50 pct SOLIDS					
1,000....	2.0	310	62	64	76
1,500....	1.1	360	90	87	98
2,000....	.7	360	91	88	97
2,500....	.3	360	92	75	99

[1]Conditions: 100 g of minus 35-mesh sample leached at 75° C for 18 h.

TABLE 9. - Effect of time on acid leaching of Conda and Fort Hall ore samples[1]

Solids, pct	Duration, h	Terminal		Extraction, pct		
		pH	emf, mV	V_2O_5	U_3O_8	P_2O_5
CONDA ORE						
50.....	3	0.7	300	80	88	96
	6	1	340	80	87	97
	18	1.1	360	90	87	98
	24	1.1	360	89	87	99
FORT HALL ORE						
40.....	3	0.8	300	68	79	95
	6	.8	330	73	86	90
	18	.8	340	78	74	89
	24	.8	360	84	87	96

[1]Conditions: 100 g of minus 35-mesh sample leached at 75° C using 1,500 lb/st H_2O_4.

TABLE 10. - Acid leaching of phosphorite ores and concentrate[1]

H_2SO_4, lb/st	Terminal		Extraction, pct		
	pH	emf, mV	V_2O_5	U_3O_8	P_2O_5
CONDA ORE					
1,500....	1.3	370	86	88	97
2,000....	.5	350	94	88	98
2,500....	.2	370	90	75	98
FORT HALL ORE					
1,000....	1.2	350	58	64	81
1,500....	.9	340	78	74	89
2,000....	.4	333	73	66	80
2,500....	.2	340	78	71	93
CONDA (HIGH-Mg) MATERIAL					
1,500....	0.9	320	86	84	93
2,000....	.6	335	91	85	96
2,500....	0	370	95	85	98
CONDA CONCENTRATE					
1,500....	1.3	165	89	76	90
2,000....	.5	260	98	78	99
2,500....	.3	360	98	23	99

[1]Conditions: 100 g of minus 35-mesh sample leached at 75° C for 18 h at 40 pct solids.

Conda (High-Mg) Material

The best extractions from this material were 95, 85, and 98 pct of the V_2O_5, U_3O_8, and P_2O_5, respectively (table 10). These results were achieved by leaching the material at 40 pct solids for 18 h at 75° C using 2,500 lb/st H_2SO_4.

Conda Concentrate

The best extractions from the Conda concentrate were 98, 78, and 99 pct of the V_2O_5, U_3O_8, and P_2O_5, respectively (table 10). These results were achieved by leaching the concentrate at 40 pct solids for 18 h at 75° C using 2,000 lb/st H_2SO_4. This should be similar to the actual mill result.

ROAST AND SALT-ROAST LEACHING

Because roast-leach methods have been effective in treating uranium ore in which the uranium could not be extracted by leaching alone, and because salt-roasting has been a viable process used in vanadium extraction (11), tests were performed to determine if vanadium and uranium extractions could be improved by these methods.

In roast-leaching, the samples were roasted for 4 h at 500° or 800° C; in salt-roasting, the samples were first combined with 10 pct NaCl, then roasted for 4 h at 800° C only. After roasting (or salt-roasting), the calcines were leached at 75° C for 18 h with additions of 1,000 to 2,500 lb/st H_2SO_4. Calcines from the Conda and Fort Hall ores were leached at 40 and 50 pct solids; calcines from the Conda (high-Mg) ore and Conda concentrate were leached at 40 pct solids.

Conda Ore

The following tabulation (from tables 7 and 11) shows that 500 lb/st less acid produced almost identical extraction levels following roasting or salt-roasting than from leaching alone.

	Leaching alone	Roast-leach	Salt-roast and leach
Conditions:			
Roast temperature.....°C..	NAp	800	800
Leach temperature.....°C..	90	75	75
Acid addition.....lb/st..	2,000	1,500	1,500
Solids content.....pct..	40	50	40
Extraction, pct:			
V_2O_5.....	97	99	97
U_3O_8.....	87	88	89
P_2O_5.....	99	98	99

NAp Not applicable.

TABLE 11. - Roast leaching and salt-roast leaching of Conda ore[1]

Solids, pct	Roast temp, °C	H_2SO_4, lb/st	Terminal		Extraction, pct		
			pH	emf, mV	V_2O_5	U_3O_8	P_2O_5
ROAST LEACH							
40.....	500	1,000	1.9	360	83	75	70
	800	1,000	1.5	340	80	77	61
	500	1,500	1	360	89	88	94
	800	1,500	1.1	400	97	88	98
	500	2,000	.3	360	94	89	96
	800	2,000	.4	352	97	88	99
50.....	800	1,000	1.8	305	80	78	60
	500	1,500	1.1	270	94	87	82
	800	1,500	.9	290	99	88	98
	800	2,000	0	391	93	77	85
SALT-ROAST LEACH USING 10 wt pct NaCl							
40.....	800	1,000	1.7	690	83	78	62
	800	1,500	1.1	700	97	89	99
	800	2,000	0	800	91	87	94
50.....	800	1,000	1.5	696	66	77	63
	800	1,500	.8	760	97	88	96
	800	2,000	0	773	95	75	96

[1]Conditions: Charges roasted for 4 h and calcines leached at 75° C for 18 h.

Fort Hall Ore

Roasting with or without salt increased V_2O_5 extractions (tables 7 and 12), as shown in the following tabulation:

	Leaching alone	Roast-leach		Salt-roast and leach	
	(1)	(2)	(3)	(4)	(5)
Conditions:					
Roast temperature.....°C..	NAp	500	800	800	800
Leach temperature.....°C..	90	75	75	75	75
Acid addition.....lb/st..	1,500	1,500	1,500	1,500	2,000
Solids content.....pct..	40	50	40	40	50
Extraction, pct:					
V_2O_5.....	89	97	96	98	99
U_3O_8.....	89	88	91	90	78
P_2O_5.....	98	97	99	99	99

NAp Not applicable.

As can be seen, salt-roasting produced slightly higher V_2O_5 values, but surprisingly, leaching the salt-roasted calcine lowered the U_3O_8 extraction considerably at the higher acid and solids content. (See columns 4 and 5 above.) Values are nearly as high after roasting without salt at only 500° C and 50 pct solids. Note that roasting enabled leaching the ore at 50 pct solids.

Conda (High-Mg) Material

Nearly identical results (tables 10 and 13) were achieved following roasting and salt-roasting at 800° C as with leaching alone, but with lower acid additions, as shown in the following tabulation:

	Leaching alone	Roast-leach	Salt-roast and leach
Conditions:			
Roast temperature.....°C..	NAp	800	800
Leach temperature.....°C..	75	75	75
Acid addition.....lb/st..	2,500	1,500	2,000
Solids content.....pct..	40	40	40
Extraction, pct:			
V_2O_5.....	95	97	96
U_3O_8.....	85	84	85
P_2O_5.....	98	97	98

NAp Not applicable.

TABLE 12. - Roast leaching and salt-roast leaching of Fort Hall ore[1]

Solids, pct	Roast temp, °C	H_2SO_4, lb/st	Terminal		Extraction, pct		
			pH	emf, mV	V_2O_5	U_3O_8	P_2O_5
ROAST LEACH							
40.....	500	1,000	1.4	350	85	89	83
	800	1,000	1.3	500	94	80	82
	500	1,500	.7	360	88	89	92
	800	1,500	.9	460	96	91	99
	500	2,000	.9	380	96	88	99
	800	2,000	.4	470	95	90	98
50.....	800	1,000	1.5	485	93	81	86
	500	1,500	.7	310	97	88	97
	800	1,500	.5	640	97	88	99
	500	2,000	.9	380	96	89	99
	800	2,000	.2	410	94	67	70
SALT-ROAST LEACH USING 10 wt pct NaCl							
40.....	800	1,000	1.4	665	92	79	80
	800	1,500	.8	700	98	90	99
	800	2,000	.3	760	97	89	99
50.....	800	1,000	1.2	770	88	81	81
	800	1,500	.5	730	98	87	97
	800	2,000	.1	780	99	78	99

[1]Conditions: Charges roasted for 4 h and calcines leached at 75° C for 18 h.

Salt-roasting and leaching with 1,500 lb/st H_2SO_4 produced even higher V_2O_5 extraction (of 98 pct), but P_2O_5 extractions were much lower (78 pct) (table 13).

Conda Concentrate

The major benefit from roasting or salt-roasting this material was an 11-pct gain in U_3O_8 extraction, under essentially the same leaching conditions as for leaching alone. There was no apparent benefit with regard to lowering acid requirements, as shown in tables 10 and 13.

	Leaching alone	Roast-leach	Salt-roast and leach
Conditions:			
Roast temperature.....°C..	NAp	800	800
Leach temperature.....°C..	75	75	75
Acid addition.....lb/st..	2,000	2,000	2,000
Solids content.....pct..	40	40	40
Extraction, pct:			
V_2O_5.....	98	98	98
U_3O_8.....	78	89	89
P_2O_5.....	99	98	97

NAp Not applicable.

TABLE 13. - Roast leaching and salt-roast leaching of Conda (high-Mg) material and Conda concentrate[1]

NaCl in roast, wt pct	H_2SO_4, lb/st	Terminal		Extraction, pct		
		pH	emf, mV	V_2O_5	U_3O_8	P_2O_5
CONDA (HIGH-Mg) MATERIAL						
0.....	1,500	1.2	440	97	84	97
	2,000	.4	390	95	86	94
	2,500	0	410	94	72	85
10.....	1,000	1.5	618	61	65	39
	1,500	1	700	98	87	78
	2,000	.1	760	96	85	98
CONDA CONCENTRATE						
0.....	1,500	0.8	310	92	89	95
	2,000	.5	340	98	89	98
	2,500	.1	440	98	88	93
10.....	1,500	.9	715	98	81	96
	2,000	.2	780	98	89	97
	2,500	0	820	98	88	99

[1]Conditions: Charges roasted at 800° C for 4 h and calcines leached for 18 h at 75° C at 40 pct solids.

LEACHING UNDER PRESSURE

Leaching tests were performed under pressure to determine if improved vanadium and uranium extraction could be achieved without affecting phosphate extraction and to determine the conditions required for optimum extractions.

Conda ore, Fort Hall ore, Conda (high-Mg) ore, and Conda concentrate samples were pressure leached in a 2-L, glass-lined Parr[5] pressure vessel. The 50-g charges were leached for 3 h at 20 pct solids under an oxygen atmosphere. The total pressure, temperature, and acid addition levels were varied. Combinations of temperature and pressure were 90° C, 50 psi; 140° C, 90 psi; and 200° C, 260 psi. (Oxygen overpressure was 50 psi.) Acid additions were varied from 1,000 to 2,500 lb/st H_2SO_4. Test results are given in table 14.

Compared with other methods, leaching under pressure generally produced lower extractions; however, this may be due to the shortened leach time for these tests (3 h compared with 18 h for all previous test series). For two of the samples, fairly comparable results were produced at lower acid addition levels than for the 18-h leach tests--Conda ore and Conda concentrate.

[5]Reference to specific products does not imply endorsement by the Bureau of Mines.

TABLE 14. - Pressure leaching of phosphorite ores and concentrate[1]

H_2SO_4, lb/st	Temp, °C	Total pressure, psi	Terminal		Extraction, pct		
			pH	emf, mV	V_2O_5	U_3O_8	P_2O_5
CONDA ORE							
1,500.....	90	50	0.8	400	86	87	92
	140	90	.9	450	92	88	92
	200	260	.7	610	89	86	82
2,000.....	90	50	.4	390	90	88	94
	140	90	.3	415	93	87	94
	200	260	.2	550	75	73	80
FORT HALL ORE							
1,500.....	90	50	0.9	390	78	88	92
	140	90	.8	350	78	88	93
	200	260	.8	375	88	78	90
2,000.....	90	50	.6	380	81	88	93
	140	90	1	390	84	89	96
	200	260	.3	370	71	14	84
CONDA (HIGH-Mg) MATERIAL							
2,000.....	90	50	0.5	420	88	84	90
	140	90	.4	470	87	73	93
	200	260	.4	630	91	66	91
2,500.....	90	50	.8	420	90	84	99
	140	90	.2	440	91	71	99
	200	260	.5	390	91	56	94
CONDA CONCENTRATE							
1,500.....	90	50	1.2	470	91	77	89
	140	90	1.1	553	94	79	89
	200	260	1.2	618	94	88	89
2,000.....	90	50	.4	404	87	88	92
	140	90	.6	322	60	61	61
	200	260	.3	612	95	79	91

[1]Conditions: Samples leached for 3 h at 20 pct solids under 49 to 50 psi O_2.

Conda Ore

Preferred leaching conditions were 140° C, 90 psi, and 1,500 lb/st H_2SO_4; this resulted in extractions of 92, 88, and 92 pct, respectively of the V_2O_5, U_3O_8, and P_2O_5 (table 14). Acid requirement was 500 lb/st less than with leaching alone.

Fort Hall Ore

Highest V_2O_5 extraction of 88 pct resulted from using the following conditions: 200° C, 260 psi, and 1,500 lb/st H_2SO_4 (90 and 78 pct P_2O_5 and U_3O_8, respectively); but much higher U_3O_8 and P_2O_5 extractions were obtained by leaching at 140° C, 90 psi, and acid additions of 2,000 lb/st. (See table 14.) The extractions were 84, 89, and 96 pct of the V_2O_5, U_3O_8, and P_2O_5, respectively. These extractions were higher than those from leaching alone, but lower than those from roasting plus leaching.

Conda (High-Mg) Material

Best extractions required 2,500 lb/st H_2SO_4, which is no better than from leaching alone or from roasting followed by leaching. This acid addition level at 90° C at 50 psi enabled extractions of 90, 84, and 99 pct, respectively of V_2O_5, U_3O_8, and P_2O_5.

Conda Concentrate

Preferred leaching conditions were 200° C, 260 psi, and 1,500 lb/st H_2SO_5. This resulted in extractions of 94, 88, and 89 pct, respectively of the V_2O_5, U_3O_8, and P_2O_5 (table 14).

SOLVENT EXTRACTION TESTS

Subsequently, tests were performed to investigate methods to obtain separate products of vanadium and uranium from the various leach solutions. Table 15 summarizes the results of these tests, which involved adjusting the solution emf prior to contacting the pregnant solution with extractants.

In the first step, U_3O_8 values were extracted by contacting the pregnant solution with 0.5M D2EHPA (di(2-ethlhexyl) phosphoric acid) plus 0.125M TOPO (trioctylphosphinic oxide), using a kerosene diluent. Contact was made at 25° C for 5 min at an aqueous-to-organic (A/O) ratio of 4:1 following adjustment of the emf on all aqueous samples. Depending upon the aqueous material, the emf adjustment involved oxidation, using $NaClO_3$, or reduction via addition of iron filings. The emf must be adjusted to the value given in table 15 or coextraction of V_2O_5 will occur. The only pregnant solution that would extract only U_3O_8 over a range of emf values was the pregnant solution produced from leaching Conda ore alone. The range was 500±20 mV.

TABLE 15. - Solvent extraction recovery of vanadium and uranium from phosphorite ore leach solutions

Method used to prepare filtrate	Feed solution, g/L		First contact (D2EHPA plus TOPO)			Second contact (OPAP plus IDA)	
	V_2O_5	U_3O_8	Solution, emf, mV	Extraction, pct V_2O_5	Extraction, pct U_3O_8	Solution, emf, mV	Extraction, pct V_2O_5
CONDA ORE							
Leach only.....	0.50	0.022	500	0	98	108	95
Roast-leach.....	.49	.027	491	0	99	182	96
Salt-roast and leach.....	.57	.030	490	0	97	180	87
Pressure-leach...	.32	.016	510	0	94	-60	99
FORT HALL ORE							
Leach only.....	0.48	0.026	482	0	97	205	96
Roast-leach.....	.71	.027	488	0	96	200	89
Salt-roast and leach.....	.81	.025	491	0	96	212	89
Pressure-leach...	.32	.016	515	0	94	182	99
CONDA (HIGH-Mg) MATERIAL							
Leach only.....	0.30	0.017	500	3	94	120	96
Roast-leach.....	.36	.018	478	6	94	142	97
Salt-roast and leach.....	.32	.017	480	0	94	-160	79
Pressure-leach...	.16	.007	510	13	86	-30	91
CONDA CONCENTRATE							
Leach only.....	0.29	0.017	500	0	94	70	96
Roast-leach.....	.28	.031	480	0	97	200	97
Salt-roast and leach.....	.39	.032	480	0	97	202	90
Pressure-leach...	.20	.017	510	0	94	190	98

The second step, which extracted V_2O_5 values, involved contacting the raffinate from the first contact with 0.3M OPAP (octylphenyl acid phosphate) plus 5 vol pct IDA (isodecanol), using a kerosene diluent. Contact was made for 30 min at 25° C at an A/O ratio of 1:1, following adjustment of the emf downward. The emf values are given in table 15, but in most cases V_2O_5 could be extracted when the emf was less than 212 mV.

This method generally worked for all sample solutions, but small amounts of V_2O_5 were extracted during the uranium separation step for three of the four Conda (high-Mg) material solutions (table 15). Typical single contact results (leach only for Conda ore) extracted 98 pct of the U_3O_8 and none of the V_2O_5 in the first step, and 95 pct of the V_2O_5 during the second step. In all cases the P_2O_5 remained in the raffinate.

SUMMARY AND CONCLUSIONS

Extractions of 91 to 99 pct of the V_2O_5, 78 to 89 pct of the U_3O_8, and 89 to 99 pct of the P_2O_5 were achieved by processing Conda, Conda (high-Mg) material, and Conda concentrate samples using the following methods: leaching only; roasting with or without salt, followed by leaching; and leaching under pressure. Metal extractions required 1,500 to 2,000 lb/st H_2SO_4 for all samples except the Conda (high-Mg) material, which required 2,000 to 2,500 lb/st. All tests involved leaching for 18 h except the pressure test, for which time was reduced to 3 h. Roasting was done for 4 h, with or without salt.

V_2O_5 extraction from Fort Hall ore was (1) 78 pct when the ore was leached at 75° C for 18 h, (2) 78 to 88 pct when leached under pressure for 3 h at 90° to 200° C with an oxygen overpressure of about 50 psi, and (3) 97 to 98 pct when roasted without salt at 500° or 800° C or roasted with salt at 800° C for 4 h, followed by leaching for 18 h. U_3O_8 and P_2O_5 extractions were 74 to 91 pct and 89 to 99 pct, respectively. The required acid addition for this ore was 1,500 lb/st H_2SO_4.

Preliminary solvent extraction tests showed that vanadium and uranium products could be separated from these leach solutions. Tests conducted at ambient temperature showed that when the emf of the leach solutions was adjusted to approximately 500 mV, an average of 95 pct of the U_3O_8 and none of the V_2O_5 was extracted using D2EHPA plus TOPO. Adjusting the raffinate emf to less than 200 mV and contacting with OPAP plus IDA enabled extraction of 79 pct or more of the V_2O_5 after one contact. All of the phosphate values were contained in the final raffinate, and therefore were available for H_3PO_4 production.

Work needs to be done on a continuous basis to determine the effect of impurity buildup on metal recovery. In addition, an economic evaluation must be conducted to determine which leaching procedures are cost effective.

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